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APPLICATION OF INSTRUMENTAL ANALYTICAL METHODS FOR IRON, TIN, LEAD AND ZINC IN CANNED FISH

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APPLICATION OF INSTRUMENTAL ANALYTICAL METHODS FOR IRON, TIN, LEAD AND ZINC IN CANNED FISH

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1 - Introduction

This work describes an accurate, sensitive and rapid method for determining the metallic traces (iron, tin, lead and zinc) in olive oil-preserved fish since there exists a close relationship between the cations present in canned fish and its appearance and nutrition value.

In all markets, at home and abroad, canned products must fulfill the following important points - be pleasing to the eye before and after opening of the tins, have no toxic effects and taste good.

The appearance of the tins depends chiefly on the degree of corrosion present. When there is corrosion of the tins, it is advantageous to determine the iron and tin concentrations in the canned fish, and to compare them with the average concentrations in fresh fish. In all food products lead concentrations must be carefully controlled and determined, owing to its high toxicity when absorved above certain limits. A technique was developed for zinc determination also not because it is toxic nor because it has anything to do with corrosion of the tins, but simply because it imparts a disagreable metallic taste to food.

The analytical methods developed have some importance because ac-

ceptance standards set limits for metallic traces.

2 - Method

To develop a suitable procedure for the determination of metallic traces, different techniques were studied, tried and modified as needed.

For the determination of iron the spectrophotometric method of 1, 10-phenanthroline[1][2] was used, which forms with the ferrous ion, in slightly acid media (pH 5 to 6) a strongly coloured hexacovalent complex of the type $(C_{12}H_8N_2)_3Fe^{++}$. The solutions were prepared taking all usual precautions, and a citrate buffer solution was used to keep the pH at 5,75 for clear and rapid colour development. The optical densities were read at 490 mμ. A calibration graph was plotted with theoretical corrections using standard solutions. The solutions from the canned fish were prepared as indicated under 3. C. and the optical density values were used to determine iron contents from the calibration graph.

The others cations were determined by the polarographic method.

4M ammonium chloride and 1M hydrochloric acid solutions made up the base electrolyte employed for tin determination[3][4][6]. M. Lingane[5] noticed that in this base electrolyte, tin has an excellent double step with half-wave potentials of -0.25 and -0.52 V vs. S.C.E.. The first step results from the reduction of the $SnCl_6^{-2}$ complex to the $SnCl_4^{-2}$ complex and the second one from the reduction of the $SnCl_4^{-2}$ complex to metal. The characteristics of these steps are well-suited to polarographic determination of this element. Acid media (pH=0.6) were used and the second step only obtained which is suitable for analytical purposes.

For the determination of lead[3][4] 0.1M potassium hydroxide and 0.03 M triethanolamine solutions were used as base electrolyte. An excelent quantitative step is obtained with half-wave potential of -0.83 V vs. S.C.E.. In this electrolyte iron also produced a reduction wave with half-wave potential of -0.95 V vs. S.C.E.. This step is not used for determining the iron concentration, but it can control the values found by the spectrophotometric method.

Zinc[3][4] gives a well-developed step in 1M ammonium chloride, 1M ammonium hydroxide solutions with half-wave potential of -1.25 V vs. S.C.E.. This reduction wave is suitable for the determination of zinc. In this base electrolyte cadmium and nickel produced a well-defined step with half-wave potentials of -0.8 V and -1.05 V vs. S.C.E. respectively. Thus, it is possi-

ble to detect traces of these elements in canned fish.

Linear calibration graphs of step-height against concentration were plotted from the values of polarogram curves of standard solutions of tin, lead and zinc in the respective base electrolytes.

The polarograms of the samples were used in the same way, and from the step-heights were obtained cation concentrations on the calibration graphs. In routine work was employed as reference electrode a mercury-pool anode instead of a saturated calomel electrode.

For the destruction of organic matter were tried out both the ashing method and wet-oxidation by acids[7][8] the latter being adopted because it is quicker and there is no danger of losing some of the inorganic constituents by volatilisation (Sn).

3 - Experimental

a) - Apparatus

Unicam S.P. 500 Spectrophotometer and usual accessories.
Radiometer PO4 Polarograph and usual accessories.
Beckman H2 pH meter.
Polymetrohm 45 pH meter.
Tempunit Thermostat.

b) - Reagents

All the reagents used are of analytical grade. The solutions were prepared with deionised and twice distilled water.

c) - Procedure

After opening of the tins, pH of the fish is measured and then whole of the contents (fish and olive oil) are placed and weighed (after homogenisation) in a tared mortar. Two to three 10 g samples are taken from this homogenised mass into tared Kjedhhl flasks on a hot-plate for nitric attack. Sulphonitric treatment follows. The last traces of organic matter can be destroyed by perchloric acid. Excess sulphuric acid is eliminated by carrying the heat to white fumes while water is added at intervals. The dry residue is taken up with chlorinated water to either 50 or 100 ml as needed.

These solutions are used for determination ot the various cations. For iron content 5 ml samples are taken, the pH is adjusted and the normal spectrophotometric treatment follows. For all the others cations 10 ml samples

are taken, heated to near dryness, redissolved in the specific base electrolyte and polarographed. In fig. I there are shown polarograms obtained from tin number 012C.

All tins are given a number and the observed degree of corrosion is noted.

4 - Results and discussion

About 50 tins of canned fish in olive oil, of different makes, different manufacturing dates, different tinplates and different packings, were tested.

Tables 1 and 2 show some of the obtained values for sardines and tunny-fish respectively.

All the fish that was tested had normal organoleptic characters.

Higher contents of iron and tin were observed in the more corroded and older tins, no matter the type of tinplate employed. In soldered tins lead content was higher than in edge-pressed tins.

5 - Conclusions

The method used is rapid, accurate and sensitive. As is obvious, the destruction of organic matter requires more time than the final determinations and, on the average, the tests for series of 5 tins (16 tests per tin) require about 36 hours all inclusive.

The average deviations on the results are of the order of 5%.

Using the described procedures, contents of iron, tin and zinc as low as 0.5 p.p.m., and lead as low as 1 p.p.m., can be determined.

Further work is being carried out along these lines to try and reach more conclusive results on the influence of types of packing (plate used, shape of tins and sealing methods) and the influence of manufacturing procedures and age, as well as other factors, as regards metallic contaminations.

At present some tins of fish canned 20 years ago are being tested.

Also, these techniques have been applied successfully on types of foods other than fish.

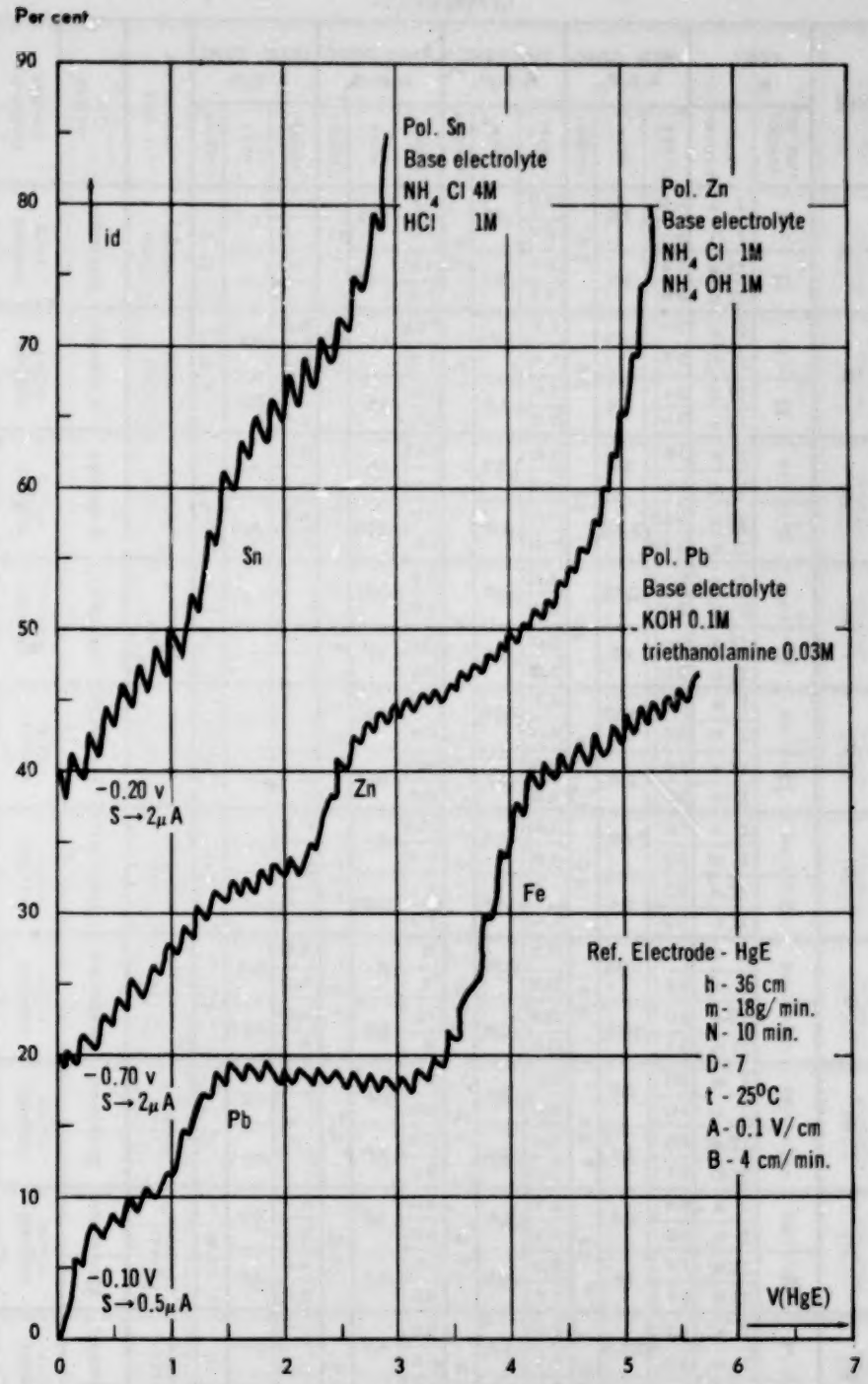

Fig. 1 - Polarograms of sample No. 012 C

TABLE 1

SAMPLE N.	TEST N.		IRON CONC. p.p.m.			TIN CONC. p.p.m.			ZINC CONC. p.p.m.			LEAD CONC. p.p.m.			MANUFACTURE DATE	TIN PATTERN	TINPLATE APPEARANCE	FISH APPEARANCE
	PREP. OF SAMPLE	TEST SAMPLE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE				
012 A	I	I a	42	39	38	2.7	2.7	2.7	13	11.5	12	—	—	< 1	AUGUST 1959	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	36			2.7			10			—						
	II	II a	38	37		2.7	2.7		13	12.5		—	—					
		II b	35			2.7			12			—						
012 B	I	I a	34	35.5	35	1.7	1.75	1.7	12.5	15	17	5.8	6.2	6.6	AUGUST 1959	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	37			1.8			18			6.5						
	II	II a	34	34		1.4	1.7		16	18		7.2	7.0					
		II b	34			2.0			20			6.8						
012 C	I	I a	38	36	35	1.8	1.9	1.7	15.5	14	15	4.0	4.9	4.5	AUGUST 1959	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	34			2.0			12			4.2						
	II	II a	33.5	33.5		1.4	1.5		17	16.5		4.9	4.8					
		II b	33.5			1.6			16			4.7						
013 A	I	I a	24	23.5	23	4.6	4.8	5	7.9	7.5	7.6	—	—	< 1	OCTOBER 1961	BLACKPLATE	SLIGHTLY CORRODED	NORMAL
		I b	23			5.0			7.9			—						
	II	II a	24	23		5.0	5.1		8.2	7.7		—	—					
		II b	22			5.2			7.2			—						
013 B	I	I a	31	30.5	29	4.1	4.05	4.1	8.6	8.5	8.7	—	—	< 1	OCTOBER 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	30			4.0			8.4			—						
	II	II a	26	28		4.0	4.1		9.0	8.9		—	—					
		II b	30			4.2			8.8			—						
013 C	I	I a	18	19	20	1.5	1.55	1.5	10.7	11	11	—	—	< 1	OCTOBER 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	20			1.6			11			—						
	II	II a	20	21		1.5	1.45		11	10.5		—	—					
		II b	22			1.4			10			—						
014 A	I	I a	31	28.5	29	0.7	0.75	0.8	9	9	9.3	4.0	4.1	4.1	AUGUST 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	26			0.8			9			4.2						
	II	II a	30	30.5		0.8	0.8		10	9.5		4.0	4.05					
		II b	31			0.8			9			4.1						
014 B	I	I a	26	28	26	2.4	24	2.4	2.2	2.5	2.7	—	—	< 1	AUGUST 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	30			2.4			2.8			—						
	II	II a	25	23		2.4	24		28	3.0		—	—					
		II b	21			2.4			32			—						
018 A	I	I a	26	26	23	1.4	1.4	1.6	50	4.9	4.8	4.1	3.5	3.6	OCTOBER 1961	ELECTROLYTIC	LITTLE CORRODED	NORMAL
		I b	26			1.3			48			3.0						
	II	II a	17	19		2.0	1.85		45	4.7		4.0	3.8					
		II b	21			1.7			48			3.6						
018 B	I	I a	27	24.5	25	1.3	1.2	1.2	50	4.9	4.8	—	—	< 1	OCTOBER 1961	ELECTROLYTIC	LITTLE CORRODED	NORMAL
		I b	22			1.1			48			—						
	II	II a	26	26		1.1	1 1		46	4.7		—	—					
		II b	26			1.1			48			—						

TABLE 2

SAMPLE N.	TEST N.		IRON CONC. p. p. m.			TIN CONC. p. p. m.			ZINC CONC. p. p. m			LEAD CONC. p. p. m			MANUFACTURE DATE	TIN PATTERN	TINPLATE APPEARANCE	FISH APPEARANCE
	PREP. OF SAMPLE	TEST SAMPLE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE	VALUES	MEAN	AVERAGE				
029 A	I	I a	27	26	25	8.2	7.9	7.7	1.2	1.3	1.3			< 1	AUGUST 1961	DIPPED PLATE	LITTLE CORRODED	NORMAL
		I b	25			7.6			1.4									
	II	II a	24	23.5		6.1	7.4		1.2	1.2								
		II b	23			8.6			1.2									
029 B	I	I a	27	26	23	8.4	8.3	8.7	1.3	1.25	1.2			< 1	AUGUST 1961	DIPPED PLATE	LITTLE CORRODED	NORMAL
		I b	25			8.2			1.2									
	II	II a	19	20		9.0	9.0		1.1	1.15								
		II b	21			9.0			1.2									
029 C	I	I a	25	24.5	24	8.0	8.5	1.1	1.2	1.2	1.2			< 1	AUGUST 1961	DIPPED PLATE	LITTLE CORRODED	NORMAL
		I b	24			9.0			1.2									
	II	II a	23	22.8		12.0	12.5		1.1	1.15								
		II b	22.5			13.0			1.2									
029 D	I	I a	24	23.5	24	8.5	8.5	7.8	1.6	1.6	1.6			< 1	AUGUST 1961	DIPPED PLATE	LITTLE CORRODED	NORMAL
		I b	23			8.5			1.6									
	II	II a	23	24		7.0	7.1		1.5	1.5								
		II b	25			7.2			1.5									
029 E	I	I a	28	27.5	28	5.0	4.9	4.9	1.7	1.6	1.7			< 1	AUGUST 1961	DIPPED PLATE	LITTLE CORRODED	NORMAL
		I b	27			4.8			1.5									
	II	II a	27	28		4.9	4.8		1.8	1.7								
		II b	29			4.7			1.6									
026 A	I	I a	24	28.5	28	1.3	1.25	1.2	12.4	11.3	11.3			< 1	OCTOBER 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	33			1.2			10.2									
	II	II a	31	27.5		1.0	1.05		11.2	11.3								
		II b	24			1.1			11.4									
026 B	I	I a	18	20	24	1.2	1.1	1.2	3.0	3.1	3.2			< 1	OCTOBER 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	22			1.0			3.2									
	II	II a	29	27		1.2	1.2		3.4	3.3								
		II b	25			1.2			3.2									
026 C	I	I a	24	22.5	24	1.9	1.8	1.7	4.7	5.65	5.2			< 1	OCTOBER 1961	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	21			1.7			6.6									
	II	II a	24	25		1.3	1.5		7.1	6.65								
		II b	26			1.7			6.2									
023 A	I	I a	12	13.5	14	2.0	2.05	2	5.6	5.35	5.6			< 1	MARCH 1962	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	15			2.1			5.1									
	II	II a	16	14.5		2.0	2.0		6.2	5.9								
		II b	13			2.0			5.6									
023 B	I	I a	14	12	13	2.1	2.1	2.1	5.4	5.3	5.2			< 1	MARCH 1962	BLACKPLATE	LITTLE CORRODED	NORMAL
		I b	10			2.1			5.2									
	II	II a	14	13.5		2.1	2.1		5.1	5.1								
		II b	13			2.1			5.1									

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